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Nanostructured catalytic hybrid materials for energy conversion or storage

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14. ABSTRACT
PI has demonstrated successful encapsulation of aluminum and oleic acid-capped aluminum (AlOA) nanoparticles into polymer and carbon nanofibers via electrospinning. Control was demonstrated over the dispersion of the nanoparticles in the matrix nanofibers: AOT and DTAB surfactants were found to be effective to make the uniform dispersion of the nanoparticles in the nanofibers. Representative AlOA nanoparticles was dispersed in nanofibers without using surfactants. PI is working on publications.

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Nanostructured catalytic hybrid materials for energy conversion or storage

PI: Kap Seung Yang (Chonnam National University)
[Other key researchers]
Prof. Hyeonseok Yoon (CNU)
Dr. Christopher Bunker (AFRL)

Objective

To investigate the reaction kinetics of energetic nanoparticles modulated by surrounding microenvironments.

The proposed project will specifically address the following topics:

(1) Explore efficient routes to confining energetic nanoparticles to a matrix via electrospinning.

(2) Identify major parameters determining energy release (reaction kinetics) from the obtained nanohybrids, and finally understand how the energy release can be controlled from materials points of view.

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Uniqueness/Impact (e.g. why is this research novel, different from what others are doing? Potential AF applications?

The unique properties of aluminum nanoparticles are related to the synthesis method, namely sonochemical approach. Therefore, we will endeavor to incorporate pre-existing energetic nanoparticles into the electrospinning process.

We can probably achieve both polymer and carbon wrappings without and with heat treatment. It is highly important to maintain the reactivity of aluminum nanoparticles and then to control their reaction kinetics by tailoring surrounding microenvironments.

Potential AF application: The aluminum nanoparticles composites can be used as a key material for controlled hydrogen production. Ultimately, a novel integrated energy generation/storage system can be constructed (see next slide)

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Accomplishments

[Reaction kinetics control of energetic nanoparticles]

- Successful encapsulation of aluminum and oleic acid-capped aluminum (AlOA) (from Dr. Bunker) nanoparticles into polymer and carbon nanofibers via electrospinning.
- Control over the dispersion of the nanoparticles in the matrix nanofibers: AOT and DTAB surfactants were found to be effective to make the uniform dispersion of the nanoparticles in the nanofibers. Representative SEM images of the resulting products are presented in Figures 1 and 2.
- AlOA nanoparticles was dispersed in nanofibers without using surfactants (Figure 3).
- Dr. Bunker has measured the enthalpy of the samples (see Figures 4, 5, and 6) and characterized them using bomb calorimetry, DSC and XRD.
- We are organizing the data to make research articles and patents.

[Iron nanoparticles for thermal management solutions]

- Iron nanoparticles encapsulated carbon nanofibers were made as a catalytic material for oxygen reduction in aviation fuels (see Figures 7 and 8).
- The iron nanoparticles were electrochemically active (see Figure 9).

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Highlights (include list of publication, recent awards).

[Publications]

(1) J. H. Kim, C. H. Kim, H. Yoon, J. S. Youm, Y. C. Jung, C. E. Bunker, Y. A. Kim, K. S. Yang, "Rationally Engineered Surface Properties of Carbon Nanofibers for the Enhanced Supercapacitive Performance of Binary Metal Oxide Nanosheets"
J. Mater. Chem. A, 2015, DOI: 10.1039/C5TA05258K

(2) Encapsulating Al nanoparticles into nanofibers: Effect of surfactant
In preparation

(3) AlOA nanoparticles embedded into nanofibers: Control on hydrogen generation kinetics
In preparation

[Patents]

We have a plan to submit patents (regarding the second and third publications) to Korea and USA soon.

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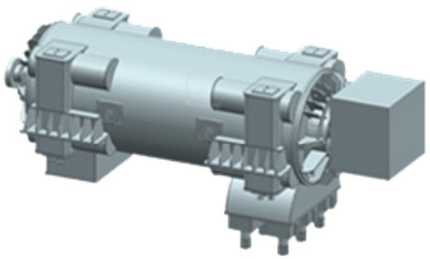
Ultimate goal: An integrated energy generation/storage system

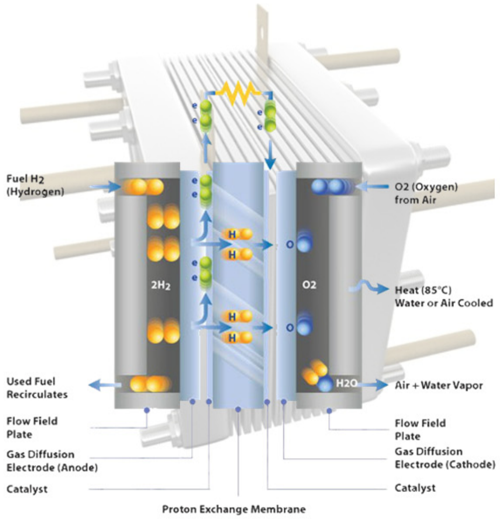
Hydrogen generator



$$2Al + 6H_2O + 2NaOH \rightarrow 2NaAl(OH)_4 + 3H_2$$
$$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3$$
$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$$

H_2

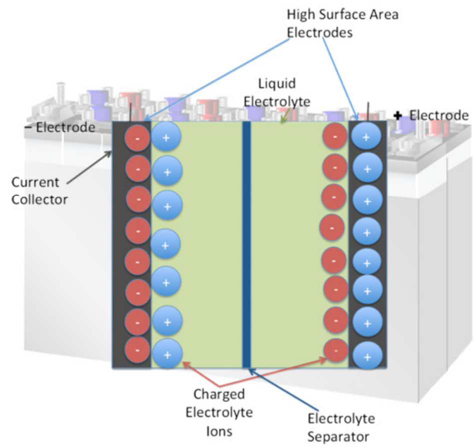
Fuel cell



e^-

e^-

Supercapacitor



The above three elements can be achieved using carbon-based materials.

Supplementary

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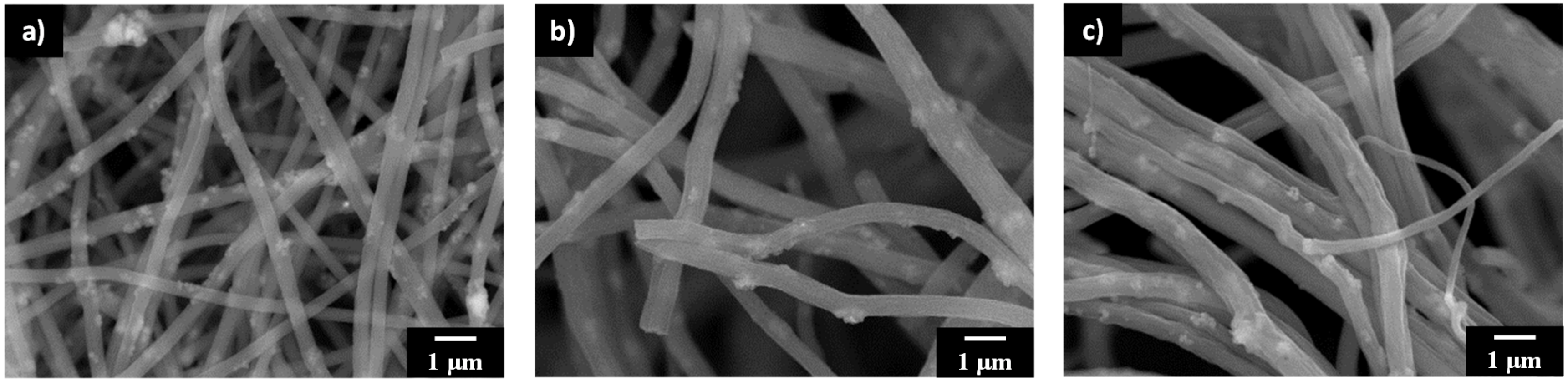
Figure 1

- SEM images of Al/PAN nanofibers containing Al nanoparticles



Al nanoparticles-encapsulated polymer nanofibers. Surfactants were used to disperse Al nanoparticles: (a) none, (b) anionic surfactant AOT, and (c) cationic surfactant DTAB.

Note that Al was mapped in the image using BEI COMPO mode.

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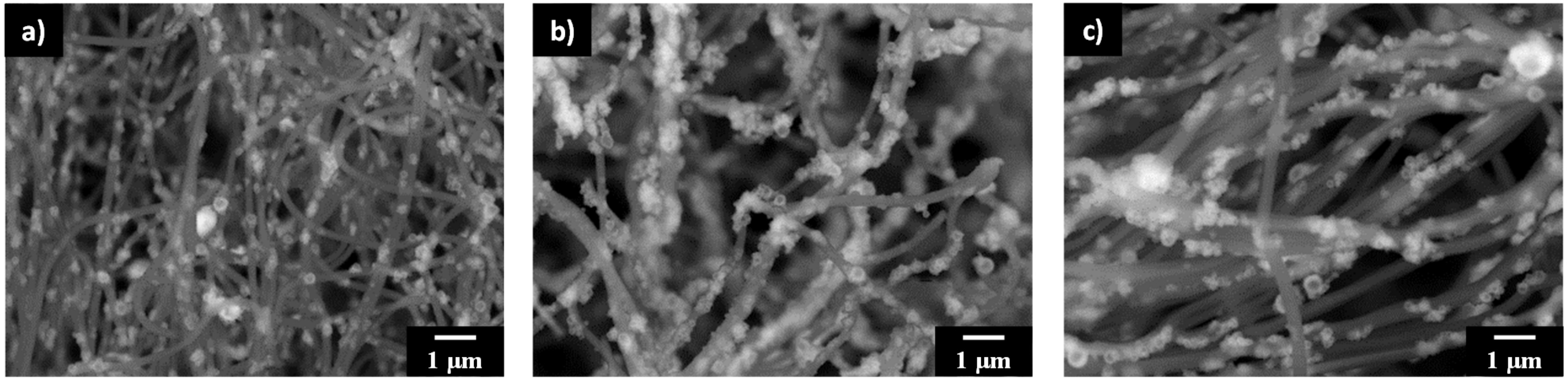
Figure 2

- SEM images of Al/carbon nanofibers containing Al nanoparticles



Al nanoparticles-encapsulated carbon nanofibers. Surfactants were used to disperse Al nanoparticles: (a) none, (b) anionic surfactant AOT, and (c) cationic surfactant DTAB.

Note that Al was mapped in the image using BEI COMPO mode.

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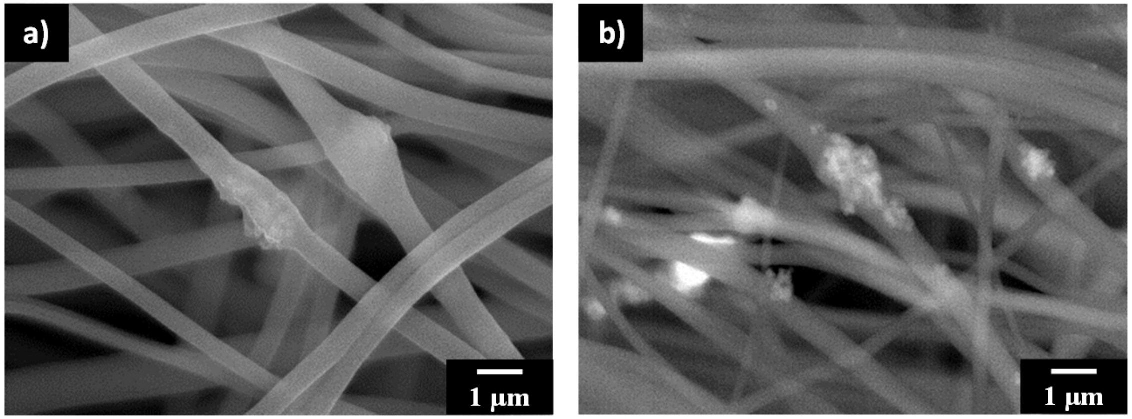
Figure 3

- SEM images of AlOA/PAN and carbon nanofibers containing Al nanoparticles



AlOA nanoparticles-encapsulated (a) polymer and (b) nanofibers. No surfactants were used to disperse Al nanoparticles.

Note that Al was mapped in the image using BEI COMPO mode.

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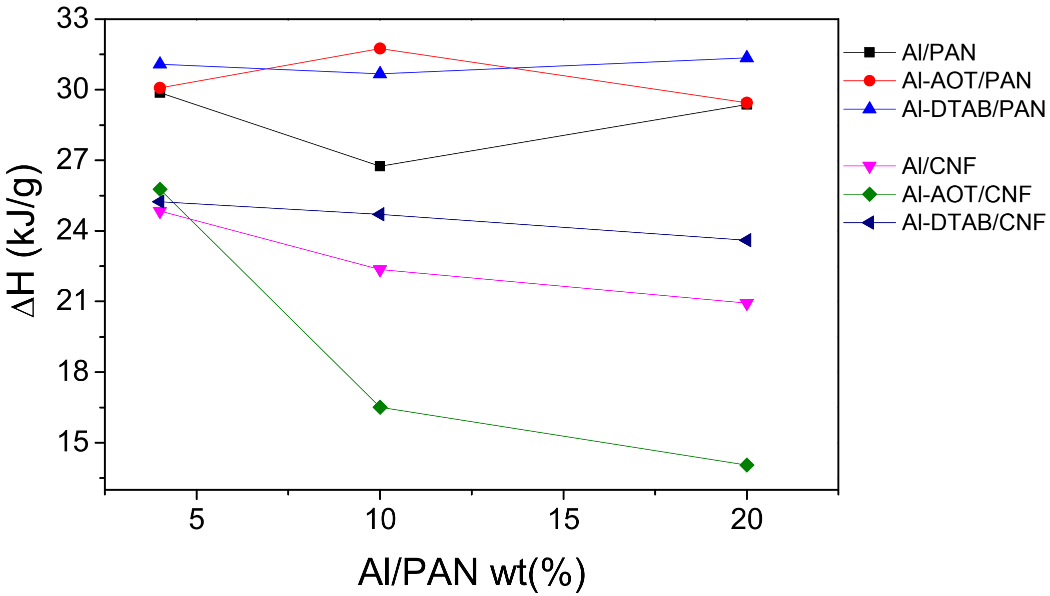
Figure 4

- **Bomb calorimeter (BC) enthalpy plot of Al-encapsulated nanofibers**

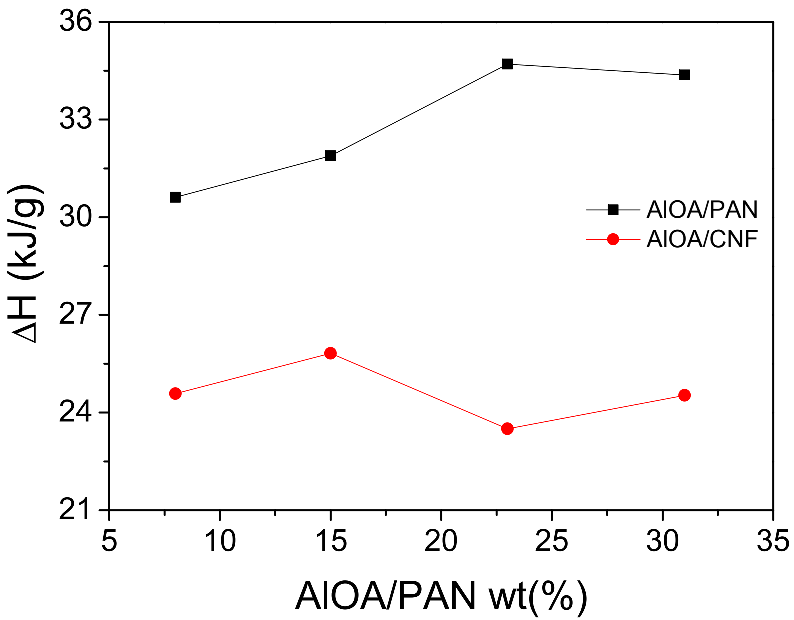


Polymer encapsulation allowed to yield higher enthalpies than carbon encapsulation.

Importantly, the enthalpy depended on the kind of surfactant used.

Figure 5

- **BC enthalpy plot of AlOA-encapsulated nanofibers**



Similarly, polymer encapsulation allowed to yield higher enthalpies than carbon encapsulation.

The enthalpy depended on the concentration of Al encapsulated.

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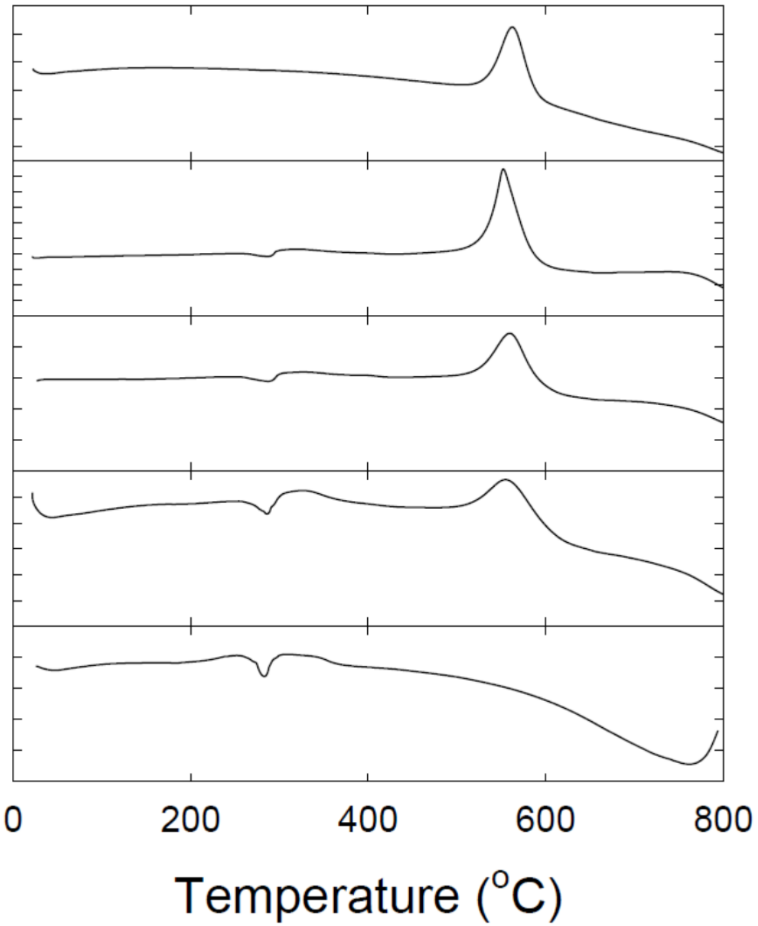
Figure 6

- DSC data for Al encapsulated nanofibers



DSC data for Al encapsulated nanofibers at Al/AOT weight ratios of 1:0, 0.4:0.6, 0.3:0.7, 0.2:0.8, and 0:1 (top: to bottom).

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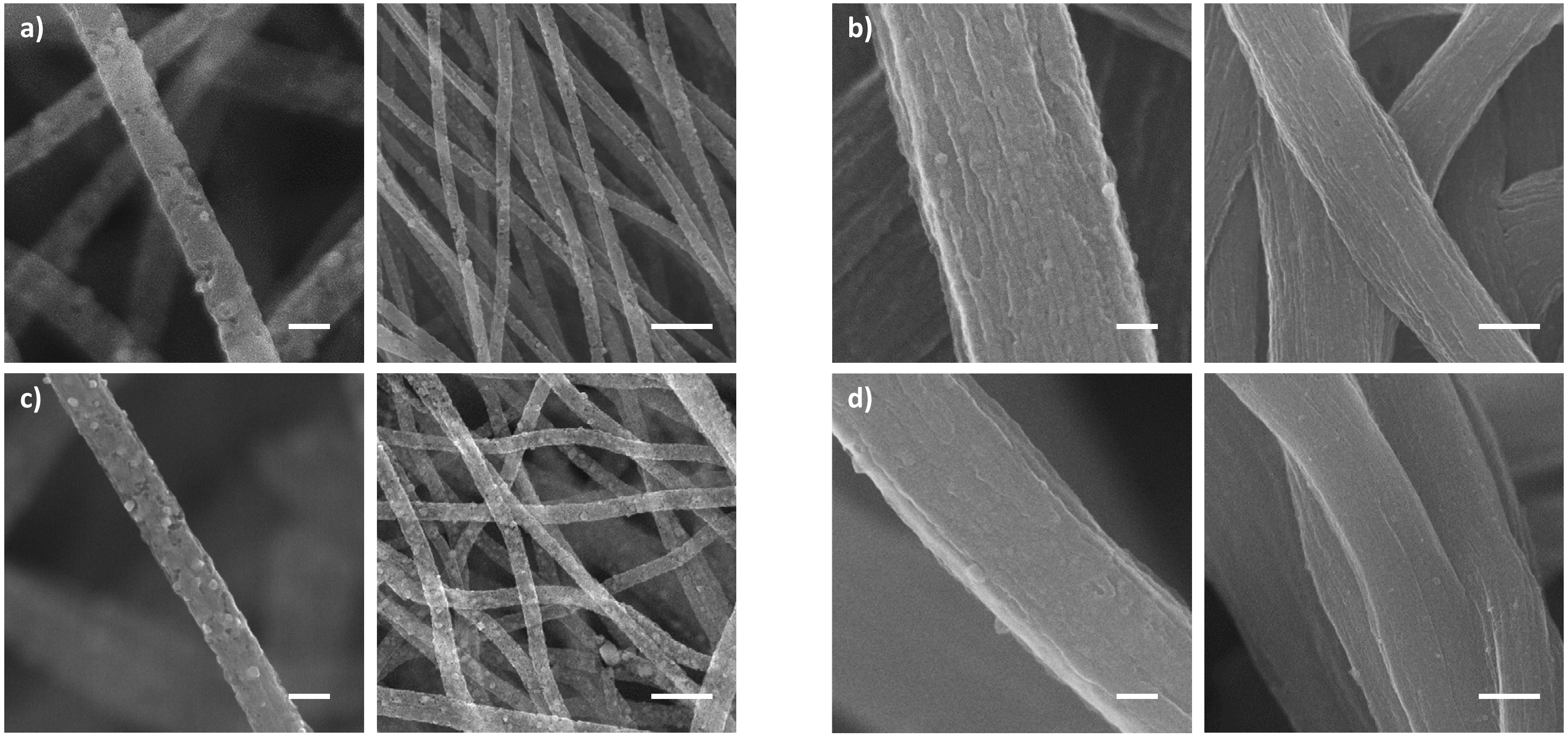
Figure 7

- **SEM images of Fe-decorated carbon nanofibers**



The carbon nanofibers were obtained with different weight percentages of three different polymer precursors (PAN:PMMA:PVP)
a) 1:0:0, b) 0.25:0.75:0, c) 0.62:0.3:0.08, d) 0.25:0.63:0.12. (Inner scale bar: left 100 nm, right 500 nm)

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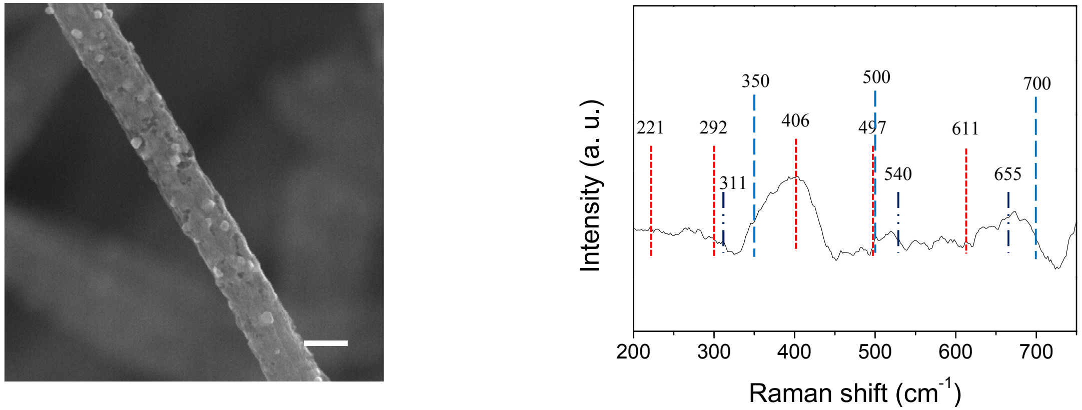
Figure 8

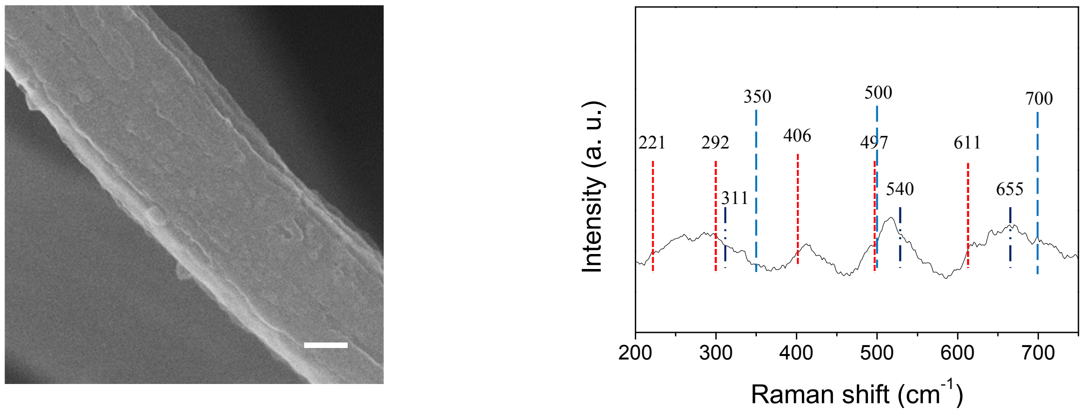
- **Raman spectroscopy analysis for Al encapsulated nanofibers**

(c)



γ-Fe_2O_3 (blue line)
α-Fe_2O_3 (Red line)
Fe_3O_4 (Black line)

(d)



α-Fe_2O_3 (Red line)
Fe_3O_4 (Black line)

Mixed iron phases: α-Fe_2O_3 and Fe_3O_4

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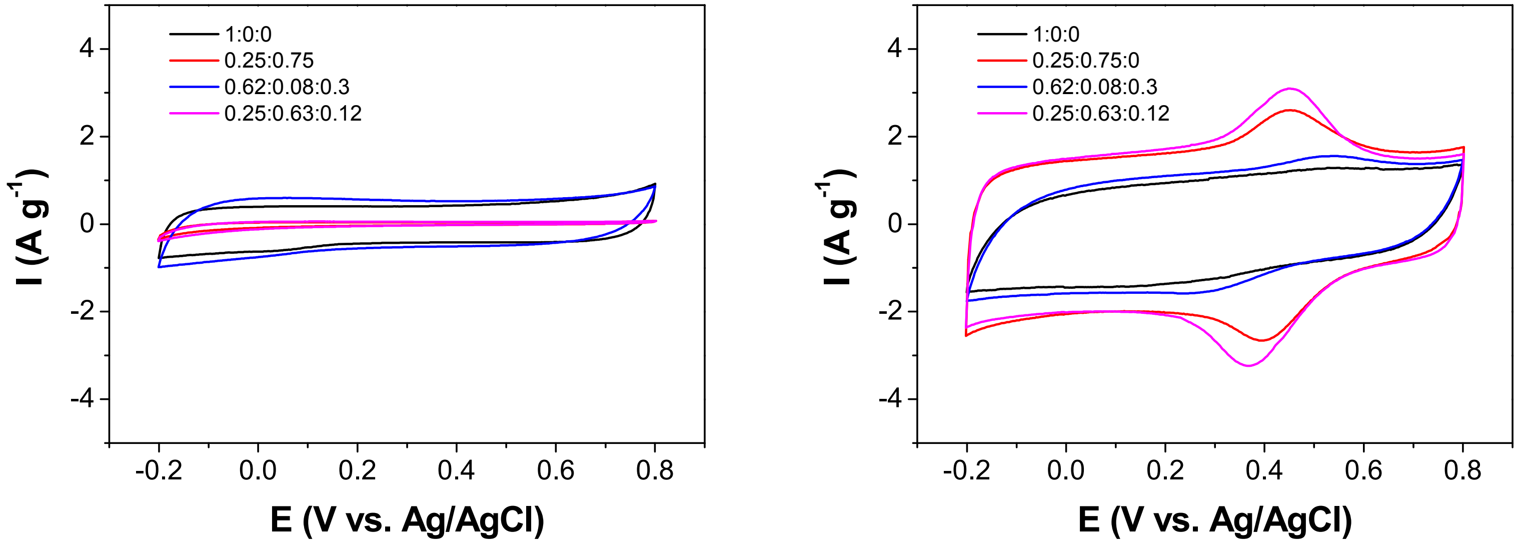
Figure 9

- **Electrochemical properties**



Electrochemical properties of CNFs with Fe. Cyclic voltammetry curves of CNFs/Fe using electrolyte of (a) Na_2SO_4 and (b) H_2SO_4 at scan rate of 25 mV s^{-1}.